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(REV 10-96)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

294-44

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/043268

INTERNATIONAL APPLICATION NO.

PCT/NL96/00362

INTERNATIONAL FILING DATE

16 September 1996

PRIORITY DATE CLAIMED

15 September 1995

TITLE OF INVENTION

Paper and Cardboard Comprising Starch- and Protein-Containing Material

APPLICANT(S) FOR DO/EO/US

Louis Peter Marie van Kessel, Gerardus Henricus Andreas Kuypers, Matheus P.M. Maessen

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A FIRST preliminary amendment.  
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:  
Copy of the International Search Report  
Copy of the International Preliminary Examination Report

**EXPRESS MAIL CERTIFICATE**

Date 03/12/98 Label No. EM331059344US  
I hereby certify that on the date indicated above, I  
deposited this paper or fee with the U.S. Postal Service,  
that it was addressed for delivery to the Assistant  
Commissioner for Patents, Washington, D.C. 20231  
by "EXPRESS MAIL Post Office to Addressee" service.

CASSANDRA LEMS  
Name (Print)

*Cassandra Lems*  
Signature

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)		INTERNATIONAL APPLICATION NO.		ATTORNEY'S DOCKET NUMBER	
		<b>PCT/NL96/00362</b>		<b>294-44</b>	

**17. ☒ The following fees are submitted:**

<b>BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):</b>	<b>930.00</b>
Search Report has been prepared by the EPO or JPO .....	<del>\$910.00X</del>
International preliminary examination fee paid to USPTO (37 CFR 1.482) .....	<b>\$700.00</b>
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) .....	<b>\$770.00</b>
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....	<b>\$1040.00</b>
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) .....	<b>\$96.00</b>

**ENTER APPROPRIATE BASIC FEE AMOUNT =**

	<b>\$</b>	<b>930.00</b>
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Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).

	<b>\$</b>	
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CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	11 - 20 =	0	X \$22.00	<b>\$</b>	
Independent claims	4 - 3 =	1	X <del>\$80.00</del>	<b>\$</b>	<b>82.00</b>
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ <del>\$200.00XX</del>	<b>\$</b>	<b>270.00</b>
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$</b>	<b>1,282.00</b>

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).

	<b>\$</b>	
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**SUBTOTAL =**

	<b>\$</b>	<b>1,282.00</b>
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Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).

	<b>\$</b>	+
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**TOTAL NATIONAL FEE =**

	<b>\$</b>	<b>1,282.00</b>
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Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **\$40.00** per property +

	<b>\$</b>	+
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**TOTAL FEES ENCLOSED =**

	<b>\$</b>	<b>1,282.00</b>
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	<b>Amount to be:</b>	<b>\$</b>
	<b>refunded</b>	
	<b>charged</b>	<b>\$</b>

a. ☒ A check in the amount of **\$ 1,282.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees.  
A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 08-2461. A duplicate copy of this sheet is enclosed.

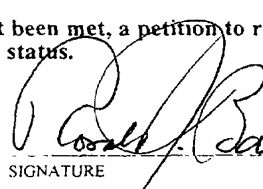
  

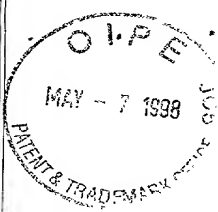
**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

Ronald J. Baron  
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 SIGNATURE  
  
 Ronald J. Baron  
 NAME  
  
 29,281  
 REGISTRATION NUMBER



75 Rec'd PCT/PTO 07 MAY 1998

17 June  
PATENT

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: Van Kessel et al.  
Serial No.: 09/043,268  
Filed: March 12, 1998  
For: PAPER AND CARDBOARD  
COMPRISING STARCH- AND  
PROTEIN-CONTAINING  
MATERIAL

Examiner: Unassigned  
Group Art Unit: 5611  
Docket: 294-44  
Dated: May 4, 1998

I hereby certify this correspondence is being deposited with the United States Postal Service as first class mail, postpaid in an envelope, addressed to: Assistant Commissioner for Patents, Washington, D.C.

Assistant Commissioner for Patents  
Washington, DC 20231  
Attn: Box Missing Parts

20231 on May 4, 1998  
Dated: 5/4/98 1 km Declaration

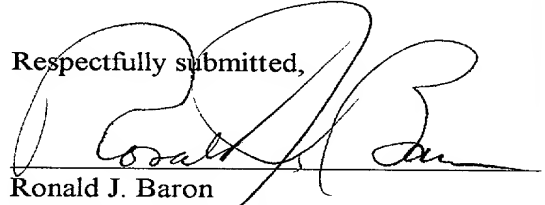
**RESPONSE TO NOTIFICATION OF MISSING  
REQUIREMENTS UNDER 35 U.S.C. § 371**

Sir:

In response to the Notification of Missing Requirements mailed April 6, 1998, Applicants enclose herewith a copy of the Notification of Missing Requirements, a Combined Declaration and Power of Attorney in compliance with 37 C.F.R. §§ 1.497(a) and (b) and a check in the amount of \$65.00 for the surcharge (payable as a Small Entity under 37 C.F.R. § 1.16(e)) associated with filing the oath or declaration on a date later than the filing date of the application. Additionally, Applicants enclose herewith for filing a Verified Statement Claiming Small Entity Status and a Recordation Form Cover Sheet with an Assignment document.

If the Office has any questions concerning this application, it is respectfully requested that an authorized official contact the undersigned attorney by telephone at the number given below.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'Ronald J. Baron', is written over a horizontal line.

Ronald J. Baron  
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Attorney for Applicants

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09/043268

Title: Paper and cardboard comprising starch- and protein-containing material

The invention resides in the field of paper and cardboard manufacturing. In particular, the invention relates to the use of a combination of starch- and protein-containing material in paper and cardboard. In fact, in this  
5 specification and the claims, the term 'paper' is meant to include cardboard as well.

Traditionally, starches are used on a large scale and in large volumes in the paper and cardboard industry. In the production of coated paper, which is substantially used as  
10 graphic paper in the fine-paper industry, it is used as, inter alia, binding agent in the coating. In general, this starch is a modified starch.

In addition, starch is used as admixture for improving the strength properties, and in particular the dry-strength  
15 properties, of the paper. For that purpose, starches conventionally used in the paper industry and anionic and cationic derivatives of these starches are used, for which reference can be made to, for instance, EP-A-0 545 228 and WO-A-94/05855.

20 In this connection, further reference can be made to Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition (1981), John Wiley & Sons, Volume 16, p. 803 ff, in particular pp. 814-819.

25 In the most current uses of starch as fiber-reinforcing component, it is either introduced - usually in the form of cationic starch - into the mass of the paper in the wet portion of the paper process, or impregnated - substantially in the form of solubilized native starch - into the paper fiber mass by means of the so-called size press.

These known strength-improving additives are advantageous, both in an economical and in a technical or technological sense; they give the paper or the cardboard an added value. Apart from providing an added value in conventional paper and cardboard processes, the need for additives for increasing the strength is enhanced in particular by the increasing use of weaker fibers, old paper that is reused more and more often, and a further increasing use of fillers instead of fibers in this old paper, resulting in a decreasing strength potential, and the decreasing availability of strong, long-fiber components in the base pulp for paper.

Actually, it is now emphasized that the invention is not limited to "waste-based" paper. The invention extends across the entire area of paper and cardboard manufacture, including paper based on "virgin fiber".

The known starch-based additives can enter into large-scale interactions with the cellulose groups of paper fibers. Thus, an increase of the number of bonds between the mutual paper fibers is formed, which reinforces the fiber-fiber bond and, accordingly, improves the strength properties of the final product.

In conventional processes wherein starches are used as strengthener, strict requirements are imposed on the protein content that may be present in the starch product used. In particular, native starch used for the manufacture of paper, substantially native wheat-, corn- or potato starch, is supplied with an additional specification for maximum protein contents of 0.3-0.5 wt.%, calculated on the dry substance. Higher protein contents are supposed to have a contaminating effect and to cause lump formation and depositions in the system. For instance, the dispersion of gluten (the protein fraction in wheat flour) leads to lumping and foam formation. These drawbacks occur to an enlarged extent when these proteins are exposed to higher temperatures in the paper manufacturing process.

The starch which forms the basic material for presently used starch additives in paper is recovered from a large number of vegetable sources, for instance from grains, such as wheat, corn and rice; from tubers, such as potatoes and  
5 tapioca; or from other plant parts, such as sago.

From the above-mentioned vegetable sources, the starch is released by the use of a combination of mechanical steps, purifying steps and drying steps. The separated protein-containing fractions, as well as other by-product fractions,  
10 are discharged. The starch purification involves the release of many waste flows, such as water flows containing biological material. These flows are increasingly becoming an environmental problem, so that draining without more is no longer possible.

The preparation of the starch that is used in the paper industry in the largest amounts as fiber-reinforcing and paper-stiffening agent, viz. wheat starch, is described as  
15 example. Similar processes are carried out for rendering starch from other vegetable sources applicable to the paper industry.  
20

Wheat grains substantially consist of two components. The core, the so-called endosperm, largely consists of starch and protein. The outer layer, the brans or the chaff, mainly contains cellulose. The ratio core:outer layer is about 80:20.

25 These wheat grains are ground, the chaff being separated from the core. The separated endosperm, consisting for about 70-80% of starch and for about 10-15% of protein, is commonly designated by the term "flour". Depending on the extraction degree of the wheat, more or less pure flour is  
30 obtained. For instance, at an extraction degree of about 80%, "grey flour" is obtained, while at a somewhat lower extraction degree of about 70%, considerably purer flour is obtained, because at this extraction degree, no parts other than the endosperm end up in the flour.

35 In the production of starch for the paper industry, the protein, in particular the gluten, is subsequently washed from the flour. The flour is thus separated into two main

components. As indicated, in this process, economically unprofitable drying steps are carried out, a part of the starting substance wheat cannot be used, and waste flows are created that have to be processed.

5       The primary object of the present invention is to provide a method wherein an optimized use is made of raw materials in the sense that a largest possible fraction of the raw material can be used in the paper process.

10       This object is realized by introducing the components of flour into the manufacturing process of paper or cardboard completely, without this flour or flour components being priorly modified by binding cationic or anionic groups thereto or without such protein/starch mixtures being priorly dry-modified. In other words, the object is realized by starting  
15       from native protein/starch mixtures and using them as such. In this specification and claims, by "flour" is meant a protein- and starch-containing fraction originating from one and the same vegetable source, or a natural mixture of protein and starch.

20       More in particular, the invention relates to paper or cardboard comprising the components of native flour in the paper fiber matrix. In addition, the invention relates to a method for manufacturing paper or cardboard wherein flour is substantially subjected to a treatment whereby starch and  
25       protein are solubilized, after which the treated components of flour are jointly introduced into the paper-fiber matrix in one step. Moreover, the invention relates to a method wherein vegetable starch sources can be used entirely, hence without generating waste products, in the paper industry.

30       Accordingly, the invention relates to paper of cardboard comprising protein and starch, at least partly originating from the same source, in the paper fiber matrix. Further, the invention relates to paper or cardboard into which all components from vegetable starch/protein sources  
35       have been processed.

It has been found that by the use of an amount of flour according to the invention, paper can be obtained which has



substantially the same properties as paper wherein about the same amount of starch is used. In other words, the function of a part of the conventionally required starch can be taken over by the protein fraction in flour, although the prior art merely teaches disadvantageous properties. In addition to economical advantages - flour is cheaper than starch prepared therefrom -, technological and environmental advantages are obtained as well, because no drying steps or purifying steps have to be carried out, and/or because no waste flows have to be discharged.

The paper according to the invention preferably comprises at least 0.1 wt.%, more preferably at least 0.3 wt.%, and usually 0.3-8 wt.% starch and at least 0.03 wt.%, preferably between 0.05 wt.% and 2.4 wt.%, usually 0.05-1 wt.% protein in the paper fiber matrix, calculated on the weight of the dry substance. If less than the minimum contents of protein and starch are used, the advantages obtained according to the present invention are too slight or other conventional auxiliary substances are required for obtaining the desired paper properties. It is true that if more than 8 wt.% starch and more than 1 wt.% protein is used, paper of a very high added value is obtained, but from a business-economical viewpoint, the process is often less attractive.

Preferably, 2-5 wt.% starch in addition to 0.2-1 wt.% protein is introduced into the paper fiber matrix, because this combines the advantages of the invention with a favorable production price.

In accordance with the present invention, the protein and starch fraction at least partly originates from one and the same vegetable source. As vegetable sources that can be used for this purpose, those having a high content of starch next to protein can be mentioned, for instance seeds, such as beans, peas and grains, for instance wheat, corn and rice grains; and other protein- and high starch-containing plant parts. In the present specification and claims, these products are designated by the term "flour".

Preferably, flour originating from grains or pulses, preferably wheat flour, is introduced into the fiber mass of the paper or cardboard. A great advantage of the use of flour originating from grains and pulses is that from an economical viewpoint, for use in accordance with the present invention, this raw material is more attractive than the starch that is normally used. For instance, at this moment, the cost of wheat flour are about half the cost of native wheat starch.

Further, because of the omission of the separation of flour into a starch and protein component, the energy consumption is reduced considerably, partly because no drying steps have to be carried out.

Flour originating from grains or pulses, and in particular wheat flour, is used in amounts of preferably 2-5% calculated on the dry mass.

Wheat flour cannot be introduced into the paper as such. If this is attempted, the drawbacks known from the prior art - high degree of deposition, lumping, dough formation, foam formation - occur. The problems prove not to occur when the flour is at least subjected to a treatment known for native starch in the paper industry.

As a skilled person knows, for use on the size press, a product dissolved in water and having a Brookfield viscosity of less than about 100 cP is required. Such a solution (it is suitable to start from a 10 wt.% flour suspension) can be obtained by treating wheat flour with a chemical and/or enzymatic starch chain-degrading agent to obtain a viscosity in the above-mentioned range. For instance, flour can be subjected to a degradation with ammonium persulfate (APS), known for native starch, optionally in the presence of an acid, for instance acetic acid or citric acid. The presence of acid in this embodiment is for instance needed if wheat flour is started from, which is illustrated in Example 2. Other methods are treatments with amylases or combinations thereof with APS, optionally complemented with a protein-modifying step.

Whereas for an interference-free size press treatment, the viscosity of native starch solutions known from the prior art is preferably between about 30 and 80 cP, a viscosity as low as only 15 cP is sufficient when flour is used. From Example 1 below, it appears that this produces a paper of the same quality as in the case where only starch is used.

In fact, it is also possible to eliminate interfering properties caused by the protein component in flour by substantially degrading this protein component and, accordingly, only utilizing the starch component effectively. However, this embodiment lacks a number of the advantages of the present invention.

Dutch patent application 1001218 describes that proteins can improve the strength properties of paper and cardboard and, in addition, have a large number of advantages when they are present in the paper fiber matrix. In particular, proteins inter alia provide, apart from improved stiffness values, SCT- ("Shortspan Compression Test"), RCT- ("Ring Crush Test"), and CMT- ("Concora Medium Test") values - and strength values - inter alia burst pressure, tensile strength -, which values are a measure for specific strength properties of the paper, in particular for the production of corrugated board, optimization possibilities and improvements in other constructional paper properties, such as stiffness, in properties of processability, such as foldability and scoring facility, and in functional properties, such as permeability to gases and liquids. Moreover, the use of proteins in paper manufacturing provides optimization possibilities and improvements in the field of general process control, usability of raw and auxiliary materials, and energy demand. Further, the above-mentioned properties can be controlled depending on the manufacturing conditions and conditions of application, for instance climatological conditions, without this being at the expense of the reprocessability of the paper product and the output of the production process.

In accordance with the present invention, it has now been found that the advantages mentioned in Dutch patent application 1001218 can also be obtained by the use of flour components in paper. For that purpose, not only the one-step treatment as known for native starch should be carried out, but a second treatment should be carried out as well. For the use of wheat flour with the size press, this second treatment is a deamidation reaction and/or a partial proteolysis. This second treatment renders the wheat gluten more water-soluble and can be carried out in a thermo-chemical manner (warming by acid) as well as in an enzymatic manner (protease).

In a preferred embodiment, the wheat flour is treated with acid APS at a temperature of about 85-95°C. In addition to the degradation of the starch, this treatment provides at the same time a processing of the protein.

As appears from the examples given below, synergistic effects occur when a starch/protein mixture prepared in an unseparated manner is used in conformity with the invention. The effect of flour on the strength and stiffness properties of paper is as great as and sometimes even greater than the effect of an approximately equally large weight fraction of conventionally treated and used, native starch.

It has been demonstrated that by introducing protein and starch molecules into the paper fiber matrix, in particular the stiffness and strength properties can be positively modified and controllably influenced.

These paper properties are not only important in respect of wrapping papers based on recirculated material, but also in respect of solid cardboard and various types of paper based on "virgin fiber".

For obtaining a good paper product, it is essential that the protein and/or starch molecules be present in the paper sheet. After all, the optimization of the fiber-fiber bond of the paper, whereby the resulting advantages can - probably - be explained, can only take place when sufficient protein and/or starch material is present on, in and between the fibers. In this manner, the paper fiber mass and the

protein and starch fraction form a whole; no clearly sharply delimited protein and starch masses and paper fiber masses are distinguished.

The advantageous effects of the use of protein in combination with starch in the bulk of the paper are dependent, sometimes even to a high degree, on the place or manner of applying and/or the nature of the protein introduced. After taking cognizance of the specification of the present invention, it will be within the scope of a skilled person to adjust the paper-manufacturing process, including the raw and auxiliary materials to be used, depending on the wishes of the customer/user and the conditions.

These above-mentioned flour-processing methods generally and mainly bring the protein fraction into solution, while the starch is solubilized and degraded. The treatment of the flour can be carried out batchwise as well as continuously-in-line.

The invention further relates to a method for manufacturing paper or cardboard, comprising at least a step wherein proteins and starch, i.e. the product as it is recovered from a natural product as unseparated vegetable protein/starch mixture, optionally after being subjected to the above-elaborated treatment analogously with the treatment carried out with native starch, is introduced into the paper fiber matrix.

In conventional paper-manufacturing processes the first treatment consists in so-called pulping - preparing pulp by suspending fiber materials in paper that may or may not have been circulated. In a large vat, by the use of mechanical energy, usually by stirring, and heating, usually with steam or warm water, fiber material is added to water. Through the mechanical and physical treatment, the fiber material is dissolved or dispersed to create a liquid mash, the pulp. Next, the pulp is subjected to a number of treatments. For instance, the pulp is cleaned, with unusable, nonfibrous material being removed from the pulp. Moreover, if necessary,

a fiber treatment, such a grinding, is carried out. Finally, the pulp is presented in a specific concentration to the paper machine which manufactures paper from the pulp.

5 In accordance with the invention, during the method for manufacturing paper, at least a step is carried out whereby proteins and starch are jointly introduced into the paper fiber matrix.

10 During the process pass from pulp vat to paper machine, auxiliary substances, including the protein-starch mixture used according to the present invention, preferably wheat flour, can be added. Moreover, after sheet formation, the protein and starch material can be provided thereon and then - by performing specific treatments - introduced into the fiber matrix.

15 For instance, during the paper sheet formation, protein-starch solutions can be introduced into the paper layer or between different paper layers, if any, for instance through spraying or foaming. Also, the protein-starch material can be introduced into the fiber mass by means of a surface treatment or impregnation of the paper already formed, for instance and preferably by means of a size press treatment. Finally, reference is made to the possibility of applying protein material to the dry paper web through spraying or other known application techniques.

25 In a preferred embodiment of the method according to the invention, protein-starch mixtures are introduced into the paper by means of a size press treatment. During the size press treatment - a treatment which is generally used in the paper industry and is therefore known to a skilled person - a solution or suspension containing the protein-starch mixture to be used is pressed into the paper by means of rolling. The size press treatment can be carried out single-sidedly on the top or bottom side of the paper web, as well as double-sidedly.

35 In particular for use in the size press, higher protein and starch concentrations have advantages with regard to the

maximally feasible properties and reduced drying energy thus required.

In the above-mentioned techniques, it is always important that at least a part of the proteins and the starch be brought into close contact with the fibers in the paper fiber matrix.

Further, it is possible to introduce, in addition to the joint introduction of a protein/starch mixture, supplementary amounts of starch or protein. This can take place at the same place by the use of the same technique, but also at other places in the paper-preparing process.

The invention relates to the use of flour components in the fiber matrix of paper for improving and directing paper properties such as strength, stiffness, permeability, surface properties and elasticity. Moreover, the flour fraction treated according to the invention can be used as glue for fixing the corrugations in corrugated cardboard.

The invention also relates to the use of protein- and starch-containing materials wherein, for attaining the desired paper properties, only the starch fraction is modified chemically or enzymatically. If the starting material contains, in addition to starch, for instance water-soluble proteins, it is not necessary to modify these proteins in order to produce a size having good processing and reinforcing properties. An example hereof is pea meal of which the proteins are soluble in an alkaline medium.-

Moreover, for reinforcing the paper, it is possible to use only the starch fraction of starch- and protein-containing materials. On the one hand, this can be effected on account of the fact that the protein, without modification, is water-soluble so that it is either pressed through the paper during the paper treatment, or, present in the paper matrix, does not contribute to the paper properties. On the other hand, the protein can be modified too far, as a consequence of which it does not contribute to the paper properties either. In the most extreme case, the protein is degraded into amino acids. An advantage hereof is that no sharply delimited processing

degree of the protein has to be set, so that the conversion of starch- and protein-containing material into the suitable size is not a very critical process.

Finally, the invention relates to a method for manufacturing paper wherein vegetable material having as main components protein and starch, preferably grain, is completely processed, comprising separating the vegetable material into (a) a fraction substantially consisting of the cellulose material and (b) a fraction substantially consisting of the protein and starch material, feeding fraction (a) to the usual starting paper fiber mass, for instance during the preparation of pulp, and feeding fraction (b) in the step wherein fiber-reinforcing additives are introduced. The fraction fed in the step wherein fiber-reinforced additives are introduced is treated in conformity with the above-described method.

In particular, in this aspect of the invention it is possible to completely grind up a vegetable protein and starch source, for instance wheat, and to use the ground-up product directly - after a modification that is analogous with native starch and optionally after a modification wherein the protein properties are optimized - as fiber-reinforcing, quality-improving component, and to use the residual products, such as the chaff, directly as fiber material. The modification of the flour can consist of a thermochemical conversion, for instance with APS and/or acid, for instance citric acid, optionally in combination with an enzymatic modification with, for instance, amylase and/or protease.

Presently, the invention will be specified with reference to the following examples.

#### Example 1

In this example, the effect of the use of flour (IJsvogel-flour, Meneba Nederland; moisture content 13.5%; about 10 wt.% gluten and about 89.5 wt.% starch calculated on the dry product) was studied. For that purpose, suspensions of flour and - for comparison - native starch were introduced into paper by means of the size press method.



The solutions of the above-mentioned macromolecules were set at a desired viscosity by subjecting both the starch fraction and the flour fraction to a degradation with ammonium persulfate (95°C). For an interference-free size press

application, the viscosity of the starch suspension should be between 30 and 80 cP; good results with the flour suspension are already obtained at a viscosity of only 15 cP.

The macromolecules-containing solutions were introduced into paper (recycled paper; D-Liner; Roermond Papier) by means of a laboratory size press (Einlehner, rate 30 m/min, temperature 70°C, pressure 2 bar).

The SCT-value and the burst factor were determined according to standardized requirements.

The SCT-value is the maximum compression force per width unit that a test strip can undergo under defined conditions until this strip becomes upset. In this example, the SCT-determination was carried out perpendicularly to the machine direction of the paper. The SCT-value is expressed in kN/m.

The burst factor is determined from a burst pressure measurement. The burst pressure is the pressure exerted on a piece of paper at the moment when the paper cracks. The burst factor (expressed in kPa) is equal to the burst pressure multiplied by 100 divided by the basic weight (g/m<sup>2</sup>).

The results are stated in the following table.

**TABLE 1** Increase of the SCT-value and the burst factor relative to the control during the use of flour or starch.

	SCT-value (kN/m)	burst factor (kPa)
starch	0.75	48
flour	0.65	42

It has been found that the use of flour gives almost the same increase in SCT-value and burst factor as starch. Moreover, a further influencing of the strength properties can be obtained by using a flour suspension having a different viscosity.

#### Example 2: pretreatments of flour slurries

##### A) treatment with neutral APS

A suspension of 694 g IJsvogel-flour in 1306 g water (50°C) was stirred in a beaker. 2.16 g APS was added, followed by stirring for another 30 minutes at 50°C. The resulting solution was diluted to a 10 wt.% solution. Heating at 75°C took place for 30 minutes, after which the whole was boiled for another 60 minutes in a water bath.

##### B) treatment with acid APS

A suspension of 232 g IJsvogel-flour in 1309 g water was stirred in a beaker. Citric acid was added to a pH of 4, after which 0.72 g APS was fed. After that, the mixture was allowed to boil for 60 minutes in a water bath.

##### C) treatment with APS and protease

A suspension of 694 g IJsvogel-flour in 1306 g water (50°C) was stirred in a beaker. 1000 µl Neutrase (NovoNordisk) was added, followed by stirring for another 30 minutes at 50°C. The resulting solution was diluted into a 10 wt.% solution. 2.16 g APS was added. The whole was boiled for 60 minutes in a water bath.

##### D) treatment with amylase and protease

A suspension of 694 g IJsvogel-flour in 1306 g water (50°C) was stirred in a beaker. 933 µl Ban α-amylase and 1000 µl Neutrase (both NovoNordisk) were added, followed by stirring for another 30 minutes at 50°C. The resulting solution was diluted to a 10 wt.% solution. For 30 minutes the temperature was increased to 75°C. After that, the whole was boiled in a water bath for another 30 minutes.

Of the four slurries A-D treated, the Brookfield viscosity was determined in cP. The measuring results are shown in the following table.

TABLE 2

		Brookfield viscosity (cP)
5	A APS -	700
	B APS citric acid	40
	C APS protease	40
	D $\alpha$ -amylase protease	25

10 The flour solutions having viscosities lower than 100 cP could readily be processed on the size press.

### Example 3

15 With a flour slurry obtained according to method D in Example 2 and a 10 wt.% standard starch slurry, test sheets (Testliner 3 Roermond Papier, 160 x 100 mm) were treated on a laboratory size press (Einlewner, rate 30 m/min, temperature 70°C, pressure 2 bar). The impregnated sheets were dried on a drying cylinder at 130°C.

20 Of these test sheets, the paper properties were determined under conditioned circumstances (23°C, 50% RV) according to standardized methods. The measuring data are stated in the following table.

**TABLE 3:** Strength and stiffness properties

paper property	starch (standard)	flour (enzymatic)	activity rel. to 100% starch
take-up (%)	3.2	3.2	
burst factor (kPa)	241	273	+13%
breaking length (m)	6454	6915	+7%
stretch (%)	1.93	2.13	+10%
SCT (140 g) (kN/m)	2.46	2.76	+12%
stiffness (kNm)	1022	1036	+1%
CMT 30 (140 g) N	278	284	+2%

In this table, "take-up" is the weight percentage flour/starch relative to the dry paper.

#### Example 4 Use of pea meal.

The proteins in pea meal are water-soluble. From pea meal, a flour size is made by modifying only the starch. In a number of experiments, the starch in pea meal is degraded by means of APS or enzymes.

TABLE 4

treatment	size viscosity (cP)	SCT-value (kN/m)
APS	150	not determined
APS + citric acid	30	4.2
BAN	80	4.2
Termamyl	60	4.4

If a suspension of pea meal is only treated with APS, the suspension obtains a high viscosity, as a consequence of which the size is difficult to apply to paper. By reducing the pH of the suspension with citric acid, the APS becomes more effective, so that a size is obtained that does meet the rheological requirements. When this size is applied to paper, the SCT-value is increased. Also the enzyme BAN and Termamyl degrade the starch sufficiently in a suspension of pea meal to obtain a viscosity lower than 100 cP. During application to paper, the SCT-value is increased.

#### Example 5: test on production scale

In a test reactor, a four slurry with enzymes (Neutrase) was suspended. Next, this slurry was thermochemically gelatinized with ammonium persulfate over a jet-cooker (NEMO-converter). On the paper machine 1 (PM1) of Roermond Papier, the flour slurry was processed on the size press.

In particular, a practical production run of the quality Testliner 3 (RP-Maasliner) in 140 g was carried out.

Machine conditions: standard, i.e.:

- composition of raw material according to formulation (recycled material);
- 2-layer embodiment;

- in-line treatment on size press;
- weight increase though size press treatment: about 3%;
- rate PM: 625 m/min;
- final moisture content paper: 7%.

During this paper production, the size press solution of native wheat starch (thermochemical conversion with ammonium persulfate (APS)) was replaced during the run by flour (IJsvogel; conversion: starch thermochemically with APS and protein part enzymatically by means of Neutrase).

Processing: good. Result comparable with 100% starch.

Paper properties: the paper properties are equal to/comparable with starch.

Depositions and foam formation resulting from gluten were not observed in the system.

**TABLE 5:** Practical test Maasliner (T.L.3), RP-PM1:

Paper properties			Starch (standard)	Flour
Gram weight	g/m <sup>2</sup>		140.1	139.9
Final moist. cont.	%		7.1	7.0
Take-up				
(size press)	%		3.2	3.1
Burst pressure	kPa		340	335
Burst factor	kPa		243	239
Breaking l. m.d.	m		6,610	6,640
Stretch m.d.	%		1.90	1.90
R.C.T. t.d.	kN/m		1.23	1.18
S.C.T. m.d.	kN/m		4.53	4.65
S.C.T. t.d.	kN/m		2.30	2.49
Stiffness m.d.	kN/m		960	940

TABLE 6: properties stated

	Paper property	Unit	Standard
1.	Gram weight	g/m <sup>2</sup>	ISO 536
2.	Moisture content	%	ISO 287
3.	Burst pressure	kPa	ISO 2758
4.	Burst factor $\left( = \frac{\text{burst pr.} \times 100}{\text{g/m}^2} \right) :$	kPa	ISO 2758
10.	S.C.T.	kN/m	DIN 54518
11.	R.C.T.	kN/m	DIN 53134
12.	C.M.T.-30	N	ISO 7263
13.	Porosity (acc. to Bendtsen)	ml/min	ISO 5636/3
8.	Stiffness	kN/m	ISO 1924/2
5.	Tensile strength	kN/m	ISO 1924/2
9.	Tearing strength	mN	ISO 1974
14.	Ply-bond (Scott-Bond)	J/m <sup>2</sup>	Tappi UM 403
7.	Stretch	%	ISO 1924/2
6.	Breaking length	km	ISO 1924/2

Note: the determinations according to 5,6,7,8,9,10,11 and 12 can be performed in the fiber direction of the paper = machine direction (m.d.) or longitudinal direction (l.d.), or in the transverse direction (t.d.).

#### Example 6

Example 5 was repeated, the flour slurry with citric acid being suspended. The results were comparable with those in Example 5.

CLAIMS

1. Paper or cardboard comprising the components of flour in the paper fiber matrix.
2. Paper or cardboard according to claim 1, comprising 0.1-8 wt.% starch and 0.3-2.4 wt.% protein in the paper fiber matrix, calculated on the weight of the dry substance.
3. Paper or cardboard according to claim 1 or 2, comprising 2-5 wt.% starch 0.2-1 wt.% protein in the paper fiber matrix.
4. Paper or cardboard according to any one of the preceding claims, wherein the components originate from agricultural products, for instance pulses and grains such as pea meal and wheat flour.
5. A method for manufacturing paper or cardboard, wherein at least flour is subjected to a treatment known in the paper industry for native starch, after which the treated components of flour are jointly introduced into the paper fiber matrix in one step.
6. A method according to claim 5, wherein the flour is treated with a chemical and/or enzymatic starch chain-degrading agent and is then introduced into the paper fiber matrix utilizing a size press.
7. A method according to claim 6, wherein the protein fraction of the flour is rendered water-soluble.
8. A method for manufacturing paper, wherein vegetable material of a high protein and starch content, preferably grain, is processed completely, comprising separating the vegetable material into (a) a fraction substantially consisting of the cellulose material and (b) a fraction substantially consisting of the protein and starch material, feeding fraction (a) to the usual fiber mass, and feeding the



fraction (b) according to any one of claims 5-7 in a step wherein fiber-reinforcing additives are introduced.

9. Use of unseparated flour components in the fiber matrix of paper or cardboard for improving or adjusting the strength properties, stiffness properties, permeability, surface properties and elasticity of the paper.
10. Use of unseparated flour components as glue for fixing the corrugations in corrugated cardboard.

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS  
(37 CFR 1.9(f) and 1.27(c)) - SMALL BUSINESS CONCERNApplicant or Patentee: L.P.M. VAN KESSEL, G.H.A. KUYPERS & M.P.M. MAESSENSerial No.: 09/043268Filing Date: 12 March 1998

Patent No.:

Issued:

For: Paper and cardboard comprising starch- and protein-containing material

I hereby declare that I am

- ☐ the owner of the small business concern identified below:  
☒ an official of the small business concern empowered to act on behalf of the concern identified below:

NAME OF CONCERN Roermond Papier B.V.ADDRESS OF CONCERN Mijnheerkensweg 18, 6041 TA Roermond, the Netherlands

I hereby declare that the above identified small business concern qualifies as a small business concern as defined in 13 CFR 121.3-18, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees under section 41(a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention, entitled Paper and cardboard comprising starch- and protein-containing material by inventor(s)

L.P.M. VAN KESSEL, G.H.A. KUYPERS & M.P.M. MAESSEN

described in

- ☐ the application filed herewith  
☒ application serial no. 09/043268, filed 12 March 1998  
☐ patent no. \_\_\_\_\_, issued \_\_\_\_\_

If the rights held by the above identified small business concern are not exclusive, each individual, concern or organization having rights to the invention is listed below\* and no rights to the invention are held by any person, other than the inventor, who could not qualify as a small business concern under 37 CFR 1.9(d) or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

\*NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

NAME \_\_\_\_\_

ADDRESS \_\_\_\_\_

☐ INDIVIDUAL ☐ SMALL BUSINESS CONCERN ☐ NONPROFIT ORGANIZATION

NAME \_\_\_\_\_

ADDRESS \_\_\_\_\_

☐ INDIVIDUAL ☐ SMALL BUSINESS CONCERN ☐ NONPROFIT ORGANIZATION

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING M.J. ClumpkensTITLE OF PERSON OTHER THAN OWNER Technical directorADDRESS OF PERSON SIGNING Mijnheerkensweg 18, 6041 TA Roermond, the Netherlands

SIGNATURE \_\_\_\_\_

DATE 25 March 1998

95122

## DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATIONS

( ) Original ( ) Supplemental ( ) Substitute (X) PCT

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; that I verily believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Title: Paper and cardboard comprising starch- and protein-containing material

which is described and claimed in:

- ( ) the attached specification, or  
 (X) the specification in the application Serial No. 09/043268 filed 12 March 1998;  
 and with amendments through \_\_\_\_\_ (if applicable),  
 (X) the specification in International Application No. PCT/NL96/00362, filed  
16 September 1996, and as amended on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the content of the above-identified specification, including the claims, as amended by any amendment(s) referred to above.

I acknowledge my duty to disclose information of which I am aware which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

COUNTRY	APPLICATION NO.	DATE OF FILING	PRIORITY CLAIMED
the Netherlands	1001218	15 September 1995	(X) YES ( ) NO
			( ) YES ( ) NO
			( ) YES ( ) NO
			( ) YES ( ) NO
			( ) YES ( ) NO
			( ) YES ( ) NO

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

SERIAL NO.	U.S. FILING DATE	STATUS
		( ) Patented ( ) Pending ( ) Abandoned
		( ) Patented ( ) Pending ( ) Abandoned
		( ) Patented ( ) Pending ( ) Abandoned

As a named inventor, I hereby appoint P.T.O.

95122 -

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RESIDENCE & CITIZENSHIP	CITY	STATE OR COUNTRY	COUNTRY OF CITIZENSHIP
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I further declare that all statements made herein of my own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

1st Inventor *[Signature]* L.P.M. van Kessel Date 25 March 1998

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5th Inventor \_\_\_\_\_ Date \_\_\_\_\_

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